MICROCOPY RESOLUTION TEST CHART

# THE EFFECT OF POTASSIUM ON THE HYDROGENATION OF CO AND $CO_2$ OVER SUPPORTED Rh CATALYSTS

BY

S. D. Worley and C. H. Dai
Department of Chemistry
Auburn University
Auburn University, AL   36849

AD-A171 553

DTIC
ELECTE
SEP 03 1986
S D
D

86  9  02  120

DTIC FILE COPY

A171 553

# REPORT DOCUMENTATION PAGE

| 1a. REPORT SECURITY CLASSIFICATION | | 1b. RESTRICTIVE MARKINGS | |
|---|---|---|---|
| Unclassified | | | |
| 2a. SECURITY CLASSIFICATION AUTHORITY | | 3. DISTRIBUTION/AVAILABILITY OF REPORT | |
| 2b. DECLASSIFICATION/DOWNGRADING SCHEDULE | | Unlimited | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S) | | 5. MONITORING ORGANIZATION REPORT NUMBER(S) | |
| 9 | | | |

| 6a. NAME OF PERFORMING ORGANIZATION | 6b. OFFICE SYMBOL (If applicable) | 7a. NAME OF MONITORING ORGANIZATION |
|---|---|---|
| Auburn University | | Office of Naval Research |
| 6c. ADDRESS (City, State and ZIP Code) | | 7b. ADDRESS (City, State and ZIP Code) |
| Department of Chemistry (Dr. S. D. Worley) Auburn University, AL 36849 | | 800 N. Quincy St. Arlington, VA 22217 |

| 8a. NAME OF FUNDING/SPONSORING ORGANIZATION | 8b. OFFICE SYMBOL (If applicable) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER |
|---|---|---|
| ONR | Code 413 | N00014-83-K-0637 |

| 8c. ADDRESS (City, State and ZIP Code) | 10. SOURCE OF FUNDING NOS. | | | |
|---|---|---|---|---|
| | PROGRAM ELEMENT NO. | PROJECT NO. | TASK NO. | WORK UNIT NO. |
| See 7b | NR 634-844 | | | |

**11. TITLE (Include Security Classification)**
The Effect of Potassium on the Hydrogenation of CO and $CO_2$ Over Supported Rh Catalysts

**12. PERSONAL AUTHOR(S)**
S. D. Worley* and C. H. Dai

| 13a. TYPE OF REPORT | 13b. TIME COVERED | | 14. DATE OF REPORT (Yr., Mo., Day) | 15. PAGE COUNT |
|---|---|---|---|---|
| Technical | FROM _____ | TO _____ | 86 July 15 | 20 |

**16. SUPPLEMENTARY NOTATION**

To be published in an ACS Symposium Series Volume on Catalytic Activation of Carbon Dioxide

| 17. | COSATI CODES | | 18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) |
|---|---|---|---|
| FIELD | GROUP | SUB. GR. | |
| | | | Infrared Spectroscopy, Methanation, CO, $CO_2$, potassium |

**19. ABSTRACT (Continue on reverse if necessary and identify by block number)**

The reactions of hydrogen with carbon monoxide and carbon dioxide over $Rh/Al_2O_3$ and $Rh/TiO_2$ films, some of which contained potassium as an additive, have been investigated. For the CO hydrogenation reaction the presence of potassium caused the dissociation or desorption of the gem dicarbonyl, linear CO, and carbonyl hydride species, while it led to an enhancement of the bridged carbonyl species. For $Rh/TiO_2$ films the hydrogenation of CO produced acetone and acetaldehyde as oxygenated products; the bridged carbonyl species was the likely precursor of these products. For the $CO_2$ hydrogenation reaction the presence of potassium caused the dissociation or desorption of all CO species, and oxygenated products were not produced. Potassium significantly poisoned both reactions toward the production of methane.

| 20. DISTRIBUTION/AVAILABILITY OF ABSTRACT | 21. ABSTRACT SECURITY CLASSIFICATION | |
|---|---|---|
| UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS ☐ | Unclassified | |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL | 22b. TELEPHONE NUMBER (Include Area Code) | 22c. OFFICE SYMBOL |
| S. D. Worley | (205) 825-4043 | |

**DD FORM 1473, 83 APR** — EDITION OF 1 JAN 73 IS OBSOLETE.

The Effect of Potassium on the Hydrogenation of CO and $CO_2$ over Supported

Rh Catalysts

S. D. Worley and C. H. Dai

Department of Chemistry, Auburn University, Auburn, AL 36849

The reactions of hydrogen with carbon monoxide and
carbon dioxide over $Rh/Al_2O_3$ and $Rh/TiO_2$ films, some of
which contained potassium as an additive, have been
investigated. For the CO hydrogenation reaction the
presence of potassium caused the dissociation or
desorption of the gem dicarbonyl, linear CO, and
carbonyl hydride species, while it led to an
enhancement of the bridged carbonyl species. For
$Rh/TiO_2$ films the hydrogenation of CO produced acetone
and acetaldehyde as oxygenated products; the bridged
carbonyl species was the likely precursor of these
products. For the $CO_2$ hydrogenation reaction the
presence of potassium caused the dissociation or
desorption of all CO species, and oxygenated products
were not produced. Potassium significantly poisoned
both reactions toward the production of methane.

COPY
INSPECTED
7

Considerable effort has been expended here toward the investigation of the CO and $CO_2$ hydrogenation reactions over supported Rh catalysts (1-4). Although for Rh/X (X = $Al_2O_3$ and $TiO_2$) at low pressure (50-100 Torr) and temperature (423-473 K) the predominant product for both of these reactions is methane (1-4), there are means of altering the product distribution toward higher hydrocarbons and/or oxygenated products such as methanol. In general it is believed that methane and higher hydrocarbons are produced from dissociated CO or $CO_2$ on supported transition metals, while undissociated CO is thought to be a precursor to oxygenated products (5). Basic support materials such as ZnO, MgO, $La_2O_3$, and $ZrO_2$ (6,7) as well as higher pressure (over 1 atm) (8,9) seem to shift the product selectivity toward oxygenates; however, $Al_2O_3$ and $TiO_2$ as support materials can also lead to oxygenated products under special conditions. For example, Goodwin and coworkers (5) have shown recently that added potassium causes the selectivity for hydrogenation of CO over 3% Rh/$TiO_2$ to shift toward oxygenated products with acetaldehyde and acetone being present in significant quantities. There has been considerable recent interest in the effects of alkali metals on catalytic reactions over single crystals (10) and over supported transition metals (5,11). This paper will report the results of recent work in these laboratories concerning the effects of potassium on the CO and $CO_2$ hydrogenation reactions over supported Rh catalytic films.

## Experimental

The Rh/$Al_2O_3$ and Rh/$TiO_2$ catalysts used in this study were prepared in a manner similar to those studied previously here (1-4,12). Briefly, acetone/water solutions containing appropriate amounts of $RhCl_3 \cdot 3H_2O$, KCl,

and alumina (Degussa Aluminum Oxide C, $100\ m^2 g^{-1}$ or titania (Degussa Titanium Dioxide P25, $50\ m^2 g^{-1}$) were sprayed using a specially designed atomizer onto a heated 20 mm $CaF_2$ infrared window. Evaporation of the solvents left a uniform thin film (typically 4.3 mg $cm^{-2}$) of the mixed solid materials adhered to the window. The window containing the film was mounted inside an infrared cell reactor (2-4) which was evacuated overnight. The sample film was then evacuated at 470 K for 1 hr, reduced at 480 K by 85 Torr doses of hydrogen for 5, 5, 10, and 20 min periods (each period followed by evacuation to ca. $10^{-5}$ Torr), and then evacuated for an additional hour at 480 K to a base pressure of $10^{-6}$ Torr. For a typical experiment the cell was then exposed to a $CO:H_2$ or $CO_2:H_2$ mixture (1:4) at ca. 82.5 Torr total pressure and heated rapidly to some prescribed temperature. Methane gas and surface intermediate formations during the reactions were monitored by infrared spectroscopy (Perkin Elmer 983 with data system) (1-4); product distributions at the end of the experiment were measured by gas chromatography (Carle 400). Pressure measurements were made with an MKS Baratron capacitance manometer (±0.01 Torr).

## Results and Discussion

## CO Hydrogenation

The interaction of CO with supported Rh catalysts has been well characterized by infrared spectroscopy (13). The primary surface species obtained are shown below. The "gem dicarbonyl" species (I) exhibits two



I           II           III
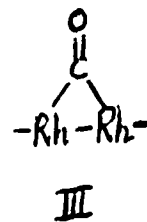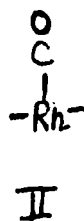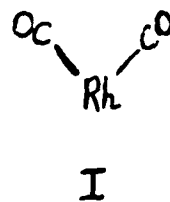
sharp infrared bands at ca. 2030 and 2100 $cm^{-1}$ which do not generally shift in wavenumber with changing surface coverage. This indicates that dipolar coupling of nearby adsorbed CO molecules is minimal for supported Rh containing predominantly this species. For Rh/X (X = $Al_2O_3$, $TiO_2$, or $SiO_2$) catalysts containing less than 1% by weight Rh, species I is the only species detected by infrared. The facts that the infrared bands for species I do not shift with coverage and that no other CO species are detected for catalysts containing low Rh loading have led some workers to suggest that species I refers to Rh in a highly dispersed state, possibly even isolated Rh atoms(12,13). Work in several laboratories (12-14) has established that Rh in species I exists in the +1 oxidation state; this probably also contributes to its tendency to remain highly dispersed. Recent work has shown that the dispersion of Rh ions in species I may be actually caused by the presence of adsorbed CO (15,16).

Figures 1 and 2 illustrate the effect of potassium on species I for a 0.5% Rh/$Al_2O_3$ catalyst film. In this experiment the two catalysts were treated identically. They were held successively at temperatures of 300, 320, 380, 430, and 460 K for 30 min at each temperature in the presence of 1 x $10^{-3}$ Torr of CO. The infrared band intensities were very similar through 380 K, probably indicating comparable CO coverages for the two samples. However, after 30 min at 430 K species I disappeared for the sample containing potassium (K: Rh = 2:1), but this phenomenon did not occur until after 30 min heating at 460 K for the sample which did not

4

contain potassium. Clearly potassium did not significantly block species I sites; rather it functioned to aid either CO bond dissociation or CO desorption from the surface, most probably through an electronic effect. The potassium may well be located on the support in close proximity to $Rh^+$ sites. Some workers have observed K/CO interactions on single crystals (17). Such interactions can give rise to low frequency CO infrared bands (1400-1800 $cm^{-1}$). A comparison of Figs. 1 and 2 indicates that such interactions do not occur appreciably for 0.5% $Rh/Al_2O_3$ catalysts which suggests that the K/CO interaction which causes enhanced dissociation or desorption of CO on or from Rh in species I may be one of long range.

When Rh/X catalysts containing higher Rh loadings (>1%) are employed, in addition to species I generally two other CO species can be detected by infrared. Species II, the "linear" species, contains one CO molecule adsorbed on a Rh atom, while species III, the "bridged carbonyl" species, contains CO bridged across two Rh atoms (13). The infrared bands for these two species shift to higher wavenumber as the CO surface coverage is increased leading most workers to suggest that these two species correspond to clusters of Rh atoms rather than highly dispersed ions as for species I. Figure 3 shows a comparison of the behavior of the CO hydrogenation reaction over 2.2% $Rh/TiO_2$ catalyst films with and without the presence of potassium. In spectrum 3a for a sample containing no potassium the four infrared bands normally observed are in evidence; the 2100 and 2030 $cm^{-1}$ bands correspond to species I, while the 2072 $cm^{-1}$ band and the broad band near 1900 $cm^{-1}$ can be assigned to species II and III, respectively. Upon heating at 440 K for 5.5 hr (spectrum 3b), species I and II disappeared, a new band was detected at 2047 $cm^{-1}$, the species III band declined in intensity, and bands corresponding to gas phase methane (3015, 1304 $cm^{-1}$)

and carbon dioxide (2349 $cm^{-1}$) were produced. The band at 2047 $cm^{-1}$ corresponds to a carbonyl hydride species rather than species II.

$$\begin{array}{c} H \diagdown \quad \diagup CO \\ Rh \end{array}$$
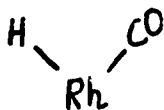
The carbonyl hydride species for supported Rh was first suggested by Solymosi and coworkers (18) and later confirmed by isotopic labeling studies here (3,4). Upon addition of potassium at 300 K (Fig. 3c), all infrared bands except the broad band for species III declined in intensity. Upon heating at 440 K for 5.5 hr (Fig. 3d), the infrared bands for species I, II, the carbonyl hydride, methane, and carbon dioxide all declined markedly in intensity relative to the identical treatment for the sample containing no potassium. Only the species III band became considerably more intense. Weak new bands at 1743, 1350, and 1220 $cm^{-1}$ which vanish upon evacuation (Fig. 3e) can be attributed to the formation of acetone; this has been confirmed by gas chromatography. Table I shows the product distributions for these experiments. Acetone and acetaldehyde were produced as oxygenated products over $Rh/TiO_2$ and to a greater extent when potassium was present. Similar results were observed for 2.2% $Rh/Al_2O_3$, ie. enhanced species III (although to less extent than noted for $Rh/TiO_2$), less species I, II, and carbonyl hydride when potassium was present; however, oxygenated products were not detected for $Al_2O_3$ as the support. Goodwin and coworkers (5) have also observed the production of comparable amounts of acetone and acetaldehyde over potassium-doped $Rh/TiO_2$ (K:Rh =

Table I. Product Distribution for CO Hydrogenation.

|  |  | Mole Percents | | | | | |
|---|---|---|---|---|---|---|---|
|  | $TN(CH_4)^a$ | $CO_2$ | $CH_4$ | $C_2H_6$ | CnHm n>2 | $CH_3CHO$ | $CH_3COCH_3$ |
| 2.2%Rh/Al$_2$O$_3$ | $1.23 \times 10^{-4}$ | 15.8 | 64.0 | 10.4 | 9.9 | ---- | ---- |
| 2.2%Rh-K/Al$_2$O$_3$ K/Rh=1 | $1.63 \times 10^{-5}$ | 33.3 | 66.6 | ---- | ---- | --- | --- |
| 2.2%Rh/TiO$_2$ | $4.20 \times 10^{-4}$ | 32.0 | 51.3 | 4.7 | 2.4 | 6.7 | 2.9 |
| 2.2%Rh-K/TiO$_2$ K/Rh=1 | $4.92 \times 10^{-5}$ | 25.7 | 42.8 | 8.6 | 0.1 | 10.8 | 12.2 |

a Turnover number for production of methane (molecules/Rh atom/sec).

1:2) although their reaction conditions were quite different (523 - 708 K, 1 - 10 atm, $CO:H_2$ = 2:1) than those here.

It is generally thought that oxygenated products in the CO hydrogenation reaction result from reaction of undissociated CO with hydrocarbon fragments (5). Since the presence of potassium appears to enhance the formation of the bridged carbonyl species III at the expense of the other species, it is likely that the bridged species is the precursor to the oxygenated products. The gem dicarbonyl species I and linear CO species II most likely dissociate at low temperature to form carbon and the carbonyl hydride species when hydrogen is present. The hydride ligand causes further dissociation of CO due to back donation of electron density into the $\pi^*$ orbital of CO. Hydrogenation of active carbon then leads to the production of methane and higher hydrocarbons. Potassium must function in several roles. It poisons the methanation reaction either by site blockage for species I, II, and the carbonyl hydride or by accelerating the production of inactive carbon through an electronic effect (electron donation into the $\pi^*$ orbital of CO). Furthermore, it accentuates the production of species III probably by steric blockage of species I and II thus enhancing the concentration of undissociated CO which can form oxygenated products.

## $CO_2$ Hydrogenation

The hydrogenation of $CO_2$ does not produce CO species I, II, and III in infrared detectable amounts. It does produce the carbonyl hydride species thus proving that $CO_2$ is dissociated over supported Rh (2-4). Figure 4 illustrates the behavior of a 2.2% $Rh/Al_2O_3$ catalyst for a series of experiments in which samples having different potassium loadings are heated

at 440 K for 5.5 hr. Note that the infrared band at 2020-2040 $cm^{-1}$ for the carbonyl hydride species is absent for all spectra shown; it was present at 300 K for the sample having no potassium, but it was greatly diminished in intensity at 300 K for the samples containing potassium, and it vanished at 300 K when the K:Rh ratio was 1.0. It is evident in the spectra shown in Fig. 4 that the amount of methane produced declined as the K:Rh ratio was increased; also, there was no spectroscopic evidence for oxygenated products.

Figure 5 shows the analogous results for $CO_2$ hydrogenation over a 2.2 % $Rh/TiO_2$ film which contained either no potassium (Fig. 5a,b) or K:Rh = 2.0 (Fig. 5c,d). The carbonyl hydride species was present (2037 $cm^{-1}$) for the sample containing no potassium, but it was absent even at room temperature for the sample containing potassium. The methanation activity was substantially decreased when potassium was present, and no oxygenated products were detected by infrared or by gas chromatography (Table II). The data in Table II show that the turnover number for methane production for $CO_2$ hydrogenation was higher in all cases for $Rh/TiO_2$ than for $Rh/Al_2O_3$, and that potassium poisoned the methanation reaction for both types of supported catalysts. Figure 6 shows that the poisoning effect was linear for both supports, but a larger slope illustrates that the effect of potassium as an additive was more dramatic for $TiO_2$. The poisoning effect was exponential as a function of potassium loading for 0.5% $Rh/Al_2O_3$.

Infrared spectroscopy indicates that there is very little CO adsorbed intact on Rh during the hydrogenation of $CO_2$. Evidently the $CO_2$ dissociates rapidly on the supported Rh catalysts to produce active carbon which is subsequently hydrogenated to methane and a smaller amount of higher hydrocarbons. The presence of potassium during the hydrogenation of

Table II.  Product Distribution for $CO_2$ Hydrogenation.

| | 2.2% Rh-K/Al$_2$O$_3$ | | | 2.2% Rh-K/TiO$_2$ | | |
|---|---|---|---|---|---|---|
| | CH$_4$ | C$_2$H$_6$ | TN(CH$_4$)$^a$ | CH$_4$ | C$_2$H$_6$ | TN(CH$_4$)$^a$ |
| K/Rh=0.0 | 89.0$^b$ | 11.0$^b$ | $3.61 \times 10^{-4}$ | 97.6$^b$ | 2.4$^b$ | $1.48 \times 10^{-3}$ |
| K/Rh=0.5 | 87.3 | 12.4 | $2.09 \times 10^{-4}$ | 96.7$^b$ | 3.3 | $1.37 \times 10^{-3}$ |
| K/Rh=1.0 | 86.4 | 13.6 | $1.62 \times 10^{-4}$ | 95.9 | 4.0 | $9.50 \times 10^{-4}$ |
| K/Rh=1.2 | ND | ND | ND | 94.5 | 5.5 | $7.98 \times 10^{-4}$ |
| K/Rh=1.5 | 86.4 | 13.6 | $1.49 \times 10^{-4}$ | 92.0 | 8.0 | $4.32 \times 10^{-4}$ |
| K/Rh=2.0 | ND | ND | $5.82 \times 10^{-5}$ | ND | ND | $2.16 \times 10^{-4}$ |

$^a$Turnover number for production of methane (molecules/Rh atom/sec).

$^b$Mole percents.

ND  No determination.

$CO_2$ does not cause an enhanced formation of bridged carbonyl species III as was the case for CO hydrogenation. Thus no oxygenated products are observed. Potassium probably poisons the methanation reacton by site blockage and by enhancing dissociation of $CO_2$ to inactive carbon.

## Conclusions

Potassium poisons the methanation reaction for both CO and $CO_2$ hydrogenation over supported rhodium. For CO hydrogenation it causes an enhanced amount of bridged species III which is not dissociated and is probably the precursor of the oxygenated products acetone and acetaldehyde. For $CO_2$ hydrogenation CO species can not be detected during the reaction when potassium is present, and oxygenated products are not detected. The effect of potassium is more dramatic for $CO_2$ hydrogenation over $Rh/TiO_2$ than over $Rh/Al_2O_3$.

## Acknowledgments

## Literature Cited

1. Worley, S. D.; Mattson, G. A.; Caudill, R. J. Phys. Chem. 1983, 87, 1671.

2. Henderson, M. A.; Worley, S. D. Surface Sci. 1985, 149, L1.

3. Henderson, M. A.; Worley, S. D. J. Phys. Chem. 1985, 89, 393.

4. Henderson, M. A.; Worley, S. D. J. Phys. Chem. 1985, 89, 1417.

5. Chuang, S. C.; Goodwin, J. G.; Wender, I. J. Catal. 1985, 95, 435.

6. Kawai, M.; Uda, M.; Ichikawa, M. J. Phys. Chem. 1985, 89, 1654.

7. Ramaroson, E.; Kieffer, R.; Kiennemann, A. J. Chem. Soc. Chem. Commun. 1982, 645.

8. Arakawa, H.; Fukushima, T.; Ichikawa, M.; Takeuchi, K.; Matsuzaki, T.; Sugi, Y. Chem. Lett. 1985, 23.

9. Poutsma, M. L.; Elek, L. F.; Ibarbia, P. A.; Risch, A. P.; Rabo, J. A. J. Catal. 1978, 52, 157.

10. For a few examples, see Somorjai, G. A. Catal. Rev. Sci. Eng. 1978, 18, 173; Somorjai, G. A. ibid 1981, 23, 189; Mross, W. D. ibid 1983, 25, 591; Peebles, D. E.; Goodman, D. W.; White, J. M. J. Phys. Chem. 1983, 87, 4378; Crowell, J. E.; Tysoe, W. T.; Somorjai, G. A. ibid 1985, 89, 1598.

11. For a few examples, see Solymosi, F.; Tombacz, I.; Koszta, J. Catal. 1985, 95, 578; Gajardo, P.; Michel, J. B.; Gleason, E. F.; McMillan, S. J. Chem. Soc. Faraday. Diss. 1979, 72, 72; Kagami, S.; Naito, S.; Kikuzono, Y.; Tamaru, K. J. Chem. Soc. Chem. Commun. 1983, 256.

12. Rice, C. A.; Worley, S. D.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. J. Chem. Phys. 1981, 74, 6487; Worley, S. D.; Rice, C. A.; Mattson, G. A.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. ibid 1982, 76, 20; Worley, S. D.; Rice, C. A.; Mattson, G. A.; Curtis, C. W.; Guin, J. A.; Tarrer, A. R. J. Phys. Chem. 1982, 86, 2714.

13. See the many references quoted in reference 12.

14. Primet, M. J. Chem. Soc. Faraday Trans. 1 1978, 74, 2570; Primet, M.; Garbowski, E. Chem. Phys. Lett. 1980, 72, 472; Primet, M.; Vedrine, J. C.; Naccache, C. J. Mol. Catal. 1978, 4, 411.

15. Van't Bilk, H. F. J.; Van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Koningsberger, D. C.; Prins, R. J. Phys. Chem. 1983, 87, 2264.

16. Solymosi, F.; Pasztor, M. J. Phys. Chem. 1985, 89, 4789.

17. See Uram, K. J.; Ng, L.; Folman, M.; Yates, J. T. _J. Chem. Phys_. 1986, 84, 2891 and the many references quoted therein.

18. Solymosi, F.; Tombacz, I.; Kocsis, M. _J. Catal_. 1982, 75, 78.

## Figure Captions

Figure 1.   Infrared spectra for the interaction of CO with a 0.5% $Rh/Al_2O_3$
film (4.0 mg $cm^{-2}$) at a background pressure of 1 x $10^{-3}$ Torr as a function
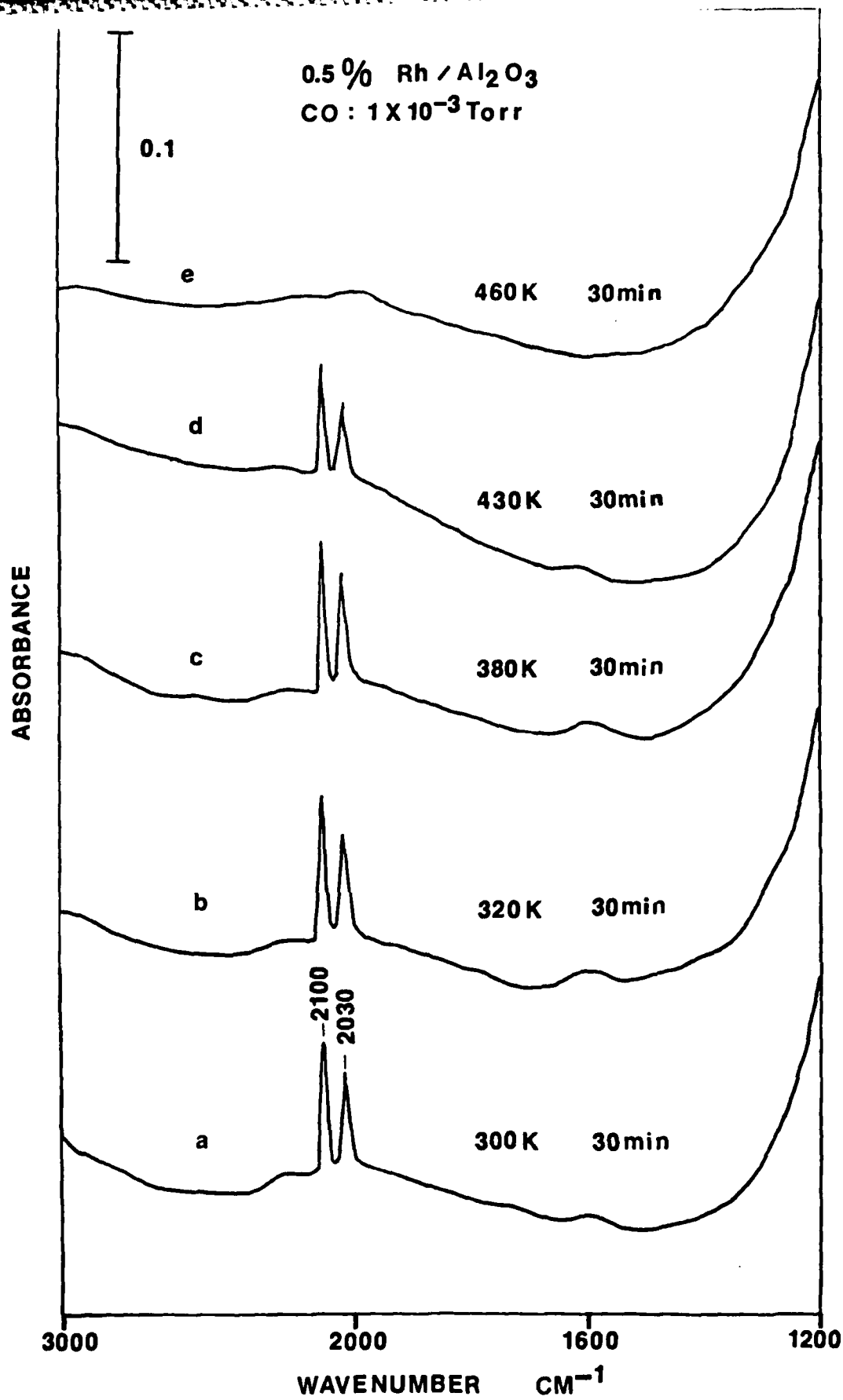of temperature.


Figure 2.   Infrared spectra for the interaction of CO with a 0.5% $Rh/Al_2O_3$
film (4.0 mg $cm^{-2}$) to which has been added potassium at K:Rh ratio of 2:1
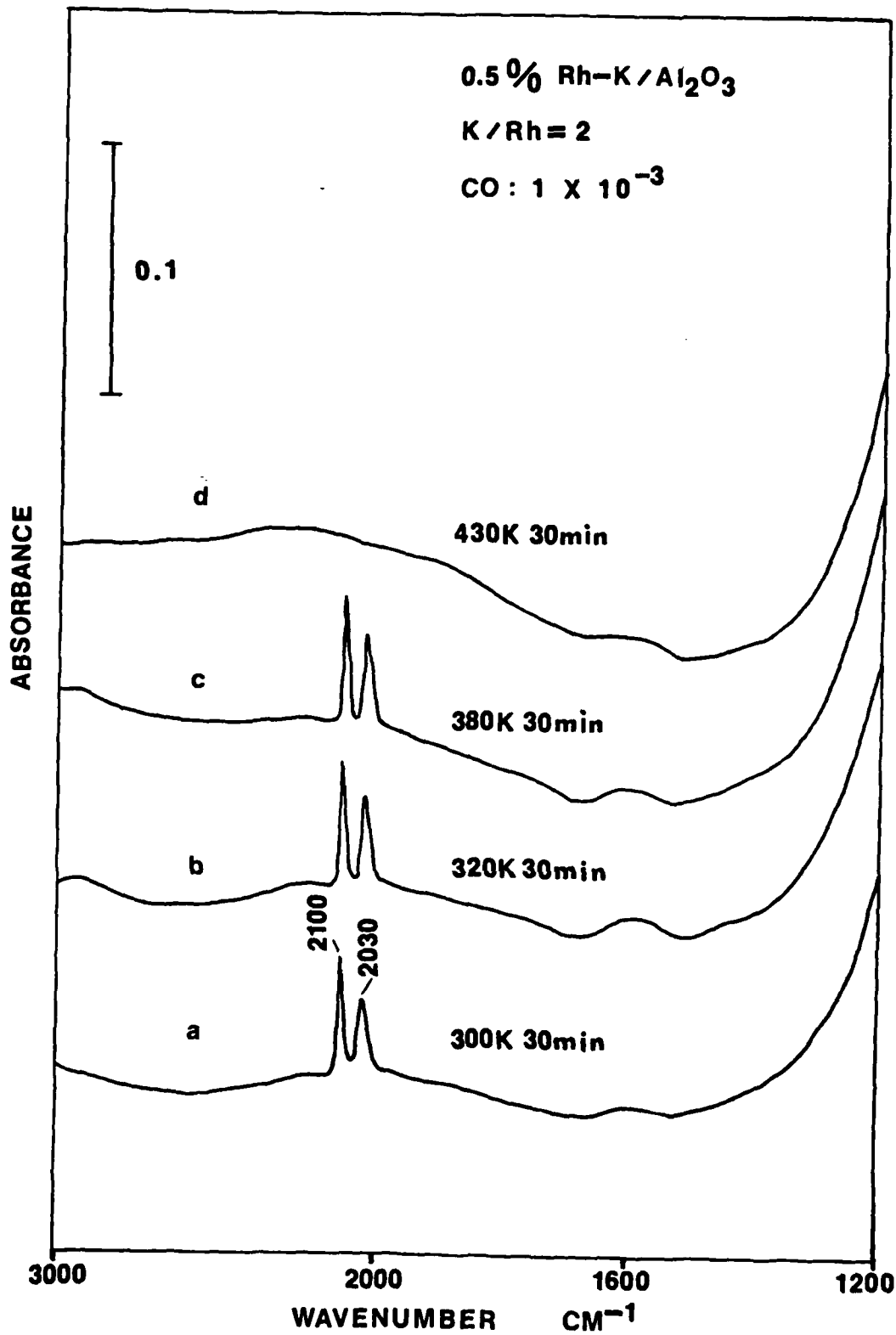at a background pressure of 1 x $10^{-3}$ Torr as a function of temperature.

Figure 3.   Infrared spectra for the interaction of $H_2$ and CO over 2.2%
$Rh/TiO_2$ films (4.3 mg $cm^{-2}$) with or without potassium added as indicated;
total pressure was 82.5 Torr.

Figure 4.   Infrared spectra for the interaction of $H_2$ and $CO_2$ over 2.2%
$Rh/Al_2O_3$ films (4.3 mg $cm^{-2}$) as a function of concentration of potassium as
an additive; total pressure was 82.5 Torr.

Figure 5.   Infrared spectra for the interaction of $H_2$ and $CO_2$ over 2.2%
$Rh/TiO_2$ films (4.3 mg $cm^{-2}$) with or without potassium added as indicated;
total pressure was 82.5 Torr.

Figure 6.   Turnover number for $CH_4$ production as a function of
concentration of potassium as an additive over 2.2% Rh/X (X = $Al_2O_3$, $TiO_2$)
films (4.3 mg $cm^{-2}$); total pressure was 82.5 Torr, and reaction temperature
was 440 K.

0.5 % Rh / Al$_2$O$_3$
CO : 1 X 10$^{-3}$ Torr

0.1

ABSORBANCE

e          460 K    30 min

d          430 K    30 min

c          380 K    30 min

b          320 K    30 min

2100
2030

a          300 K    30 min

3000        2000        1600        1200

WAVENUMBER    CM$^{-1}$

0.5 % Rh-K/Al₂O₃

K/Rh = 2

CO: 1 X 10⁻³

0.1

ABSORBANCE

d    430K 30min

c    380K 30min

b    320K 30min

2100    2030

a    300K 30min

3000    2000    1600    1200

WAVENUMBER    CM⁻¹

2.2% Rh/TiO₂
H₂/CO = 4

e — Rh–K/TiO₂ K/Rh=1 1×10⁻³ Torr
d — Rh–K/TiO₂ K/Rh=1 440K 5.5hr
c — Rh–K/TiO₂ K/Rh=1 300K
b — Rh/TiO₂ 440K 5.5hr
a — Rh/TiO₂ 300K

ABSORBANCE

WAVENUMBER CM⁻¹

Worley + Dai, Fig. 3

2.20% Rh–K/Al$_2$O$_3$

H$_2$/CO$_2$ = 4

440 K 5.5hr

K/Rh = 2.0

K/Rh = 1.5

K/Rh = 1.0

K/Rh = 0.5

K/Rh = 0.0

1304

3015

2920

0.2

e

d

c

b

a

WAVENUMBER   CM$^{-1}$

1200   1600   2000   3000   4000

ABSORBANCE

Worley + Bai, Fig. 4

2.2% Rh–K / TiO$_2$

H$_2$ / CO$_2$ = 4

cool to 300K

440K 5.5hr

cool to 300K

440K 5.5hr

1304

2000

2037

3015

2960 2920

K / Rh = 2.0

K / Rh = 2.0

K / Rh = 0.0

K / Rh = 0.0

0.2

d

c

b

a

ABSORBANCE

WAVENUMBER    CM$^{-1}$

4000    3000    2000    1600    1200

Worley & Dai, Fig. 5

CH4 molec / Rh atom / sec (×10^4)

TURNOVER NUMBER

$H_2 / CO_2 = 4$

2.2% Rh−K / TiO$_2$ : O

2.2% Rh−K / Al$_2$O$_3$ : X

K / Rh RATIO

## TECHNICAL REPORT DISTRIBUTION LIST, GEN

| | No. Copies | | No. Copies |
|---|---|---|---|
| Office of Naval Research<br>Attn: Code 413<br>800 N. Quincy Street<br>Arlington, Virginia 22217 | 2 | Dr. David Young<br>Code 334<br>NORDA<br>NSTL, Mississippi 39529 | 1 |
| Dr. Bernard Douda<br>Naval Weapons Support Center<br>Code 5042<br>Crane, Indiana 47522 | 1 | Naval Weapons Center<br>Attn: Dr. A. B. Amster<br>Chemistry Division<br>China Lake, California 93555 | 1 |
| Commander, Naval Air Systems Command<br>Attn: Code 310C (H. Rosenwasser)<br>Washington, D.C. 20360 | 1 | Scientific Advisor<br>Commandant of the Marine Corps<br>Code RD-1<br>Washington, D.C. 20380 | 1 |
| Naval Civil Engineering Laboratory<br>Attn: Dr. R. W. Drisko<br>Port Hueneme, California 93401 | 1 | U.S. Army Research Office<br>Attn: CRD-AA-IP<br>P.O. Box 12211<br>Research Triangle Park, NC 27709 | 1 |
| Defense Technical Information Center<br>Building 5, Cameron Station<br>Alexandria, Virginia 22314 | 12 | Mr. John Boyle<br>Materials Branch<br>Naval Ship Engineering Center<br>Philadelphia, Pennsylvania 19112 | 1 |
| DTNSRDC<br>Attn: Dr. G. Bosmajian<br>Applied Chemistry Division<br>Annapolis, Maryland 21401 | 1 | Naval Ocean Systems Center<br>Attn: Dr. S. Yamamoto<br>Marine Sciences Division<br>San Diego, California 91232 | 1 |
| Dr. William Tolles<br>Superintendent<br>Chemistry Division, Code 6100<br>Naval Research Laboratory<br>Washington, D.C. 20375 | 1 | | |

## ABSTRACTS DISTRIBUTION LIST, 634

Dr. K. N. Nicholas
Department of Chemistry
University of Oklahoma
Norman, Oklahoma 73019

Dr. Aaron Fletcher
Code 3852
Naval Weapons Center
China Lake, California 93555

Dr. A. Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02912

Dr. J. Cooper
Code 6130
Naval Research Laboratory
Washington, D.C. 20375

Dr. M. C. Baird
Department of Chemistry
Queen's University
Kingston, Canada
K7L 3N6

Dr. N. N. Lichtin
Department of Chemistry
Boston University
685 Commonwealth Avenue
Boston, Massachusetts 02215

Dr. R. Eisenberg
Department of Chemistry
University of Rochester
Rochester, New York 14627

Dr. N. Cooper
Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Dr. S. D. Worley
Department of Chemistry
Auburn University
Auburn, Alabama 36830

Dr. L. Vaska
Department of Chemistry
Clarkson College
Potsdam, New York 13676

Dr. R. A. Huggins
Materials Science and
    Engineering Department
Stanford University
Stanford, California 94305

END

10-86

DTIC